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(54) **Triphendioxazine compounds**

Triphendioxazinverbindungen

Composés de triphendioxazine

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(56) References cited:
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The file contains technical information submitted after the application was filed and not included in this specification

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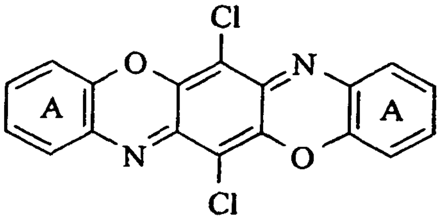
Description

[0001] The invention relates to novel chlorine-containing triphendioxazine compounds and to their use as pigments.

[0002] GB 2284427 A describes chlorine-containing, symmetrically disubstituted triphendioxazine compounds of the following general formula



where

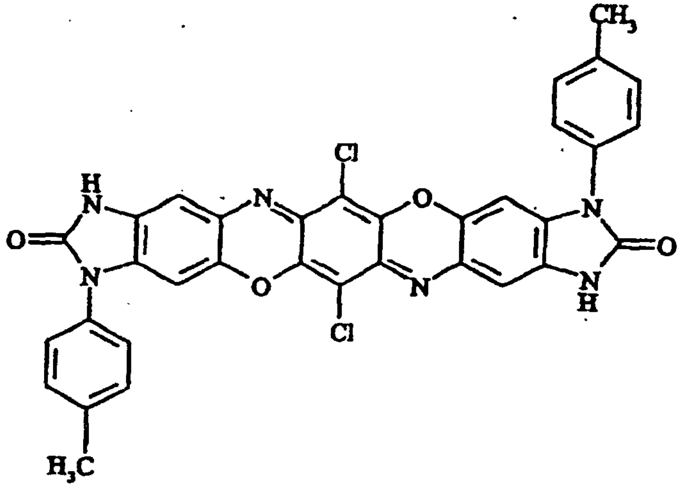
the rings labelled A carry rings which are fused linearly or angularly and consist of radical members, inter alia, of the formulae -NR_1-$(CO)_m$-NH- and -CR_1=CH-CO-NH- wherein R_1 is hydrogen, C_{1-4}alkyl or phenyl, preferably hydrogen, methyl or ethyl; and m is 1 or 2.

[0003] The preparation process disclosed in GB 2284427 A starts from intermediates i.e. amino compounds, which are ortho-substituted by an alkoxy group and are obtainable only by way of a relatively complex synthesis. The pigments disclosed in GB 2284427 A are difficultly dispersible and cannot easily be brought into pigment form.

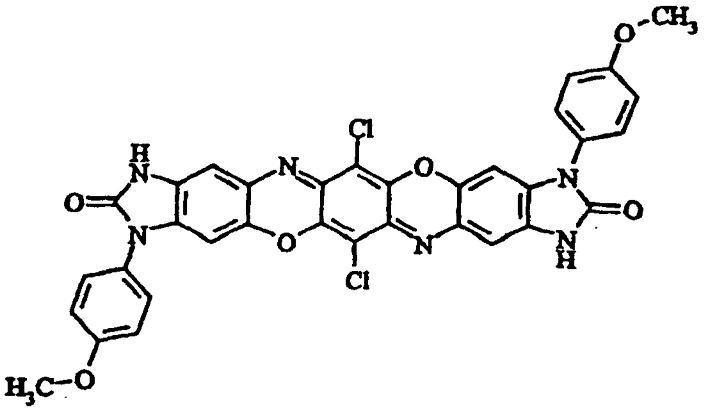
[0004] It is an object of the invention to provide new pigments possessing high fastness to solvents, migration and light, which have good thermal stabilities and a high tinting power and are also easily dispersible resp. easily to be brought into pigment form.

[0005] This object is achieved by the novel triphendioxazine compounds according to Claim 1 and their use as pigments according to Claim 2.

[0006] The present patent application therefore provides compounds of the formulae (1f) and (2f).



(1f)



(2f)

[0007] Triphendioxazine compounds of the formulae (1f) and (2f) according to the invention are used as pigments.

[0008] Aftertreating the crude pigments in organic solvents in which the pigments themselves are not dissolved and at elevated temperatures, for example at from 60 to 200°C, especially from 70 to 150°C and preferably from 75 to 100°C, can often be used to further improve the pigment properties. Aftertreatment is preferably combined with a milling or kneading operation.

[0009] The pigments according to the invention are excellently suited to the colouring of polymer compositions, by which are meant solvent-free and solvent-containing compositions comprising plastics or synthetic resins (in oil-based or water-based paints, in coating materials of various kinds, for the spin dyeing of viscose or cellulose acetate, or for pigmenting plastics, such as polyamide, polyethylene, polystyrene, polyvinyl chloride, rubber and artificial leather). They can also be used in printing inks for the graphical industry, for the colouring of paper pulps, for the coating of textile or for pigment printing.

[0010] The resulting colorations are notable for their outstanding heat, light and weather fastness, chemical resistance, colour strength and very good applications properties, examples being their crystallization fastness and dispersing fastness, and especially for their fastness to migration, bleeding, overcoating and solvents.

[0011] In addition, the pigments of the invention are also suitable as colorants in electrophotographic toners and developers, such as one- or two-component powder toners (also known as one- or two-component developers), magnetic toners, liquid toners, polymerization toners and further speciality toners (literature: L.B. Schein, "Electrophotography and Development Physics"; Springer Series in Electrophysics 14, Springer Verlag, 2nd edition, 1992).

[0012] Typical toner binders are addition polymerization, polyaddition and polycondensation resins, such as styrene, styrene-acrylate, styrene-butadiene, acrylate, polyester and phenolic-epoxy resins, polysulphones, polyurethanes, individually or in combination, and also polyethylene and polypropylene, in or to which further ingredients, such as charge control agents, waxes or flow assistants may be present or may be added subsequently.

[0013] A further area of application of pigments of the invention is their use as colorants in powders and powder coating materials, especially triboelectrically or electrokinetically sprayed powder coating materials, which are used to coat the surfaces of articles made, for example, from metal, wood, plastic, glass, ceramic, concrete, textile material, paper or rubber (J.F. Hughes, "Electrostatics Powder Coating", Research Studies Press, John Wiley & Sons, 1984).

[0014] Powder coating resins employed are typically epoxy resins, carboxyl- and hydroxyl-containing polyester resins, polyurethane resins and acrylic resins, together with customary hardeners. Combinations of resins are also used. For example, epoxy resins are frequently employed in combination with carboxyl- and hydroxyl-containing polyester resins. Examples of typical hardener components (depending on the resin system) are acid anhydrides, imidazoles and dicyandiamide and derivatives thereof, blocked isocyanates, bisacylurethanes, phenolic and melamine resins, triglycidyl isocyanurates, oxazolines and dicarboxylic acids.

[0015] The pigments of the invention are suitable, moreover, as colorants in ink-jet inks, both aqueous and non-aqueous, and in those inks which operate in accordance with the hotmelt process.

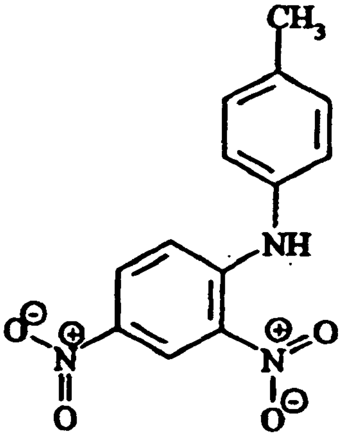
[0016] In the following examples the parts and percentages are by weight. The temperatures are indicated in degrees Celsius. One part by volume corresponds to the volume of one part by weight of water.

EXAMPLE 1

Derivatives of 1-p-tolyl-1,3-dihydrobenzimidazol-2-one

a) 2,4-dinitrophenyl-p-tolylamine

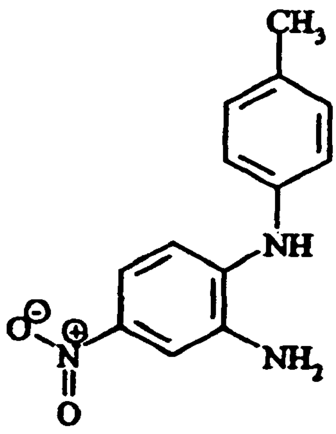
[0017] 310 parts of 2,4-dinitrochlorobenzene (98%) are suspended in 1250 parts of ethanol and the suspension is heated to 50°C. 325 parts of para-toluidine are added over 1.5 hours. The mixture is heated under reflux for 2 hours and filtered while hot, and the solid product is washed with 400 parts of hot alcohol. It is then washed with water until free from chloride. Drying under reduced pressure at 80°C gives 406 parts of red-orange needles of a compound of the following formula



Yield:	99%
Melting point:	133.6°C
IR (KBr):	3313 - 1622 - 1609 - 1581 - 1519 - 1335 cm^{-1}
MS(m/e):	273 - 256 - 229 - 226 - 210 - 196 - 180 - 168 - 152 - 139 - 127

b) 4-nitro-N-1-p-tolyl-1,2-diaminobenzene

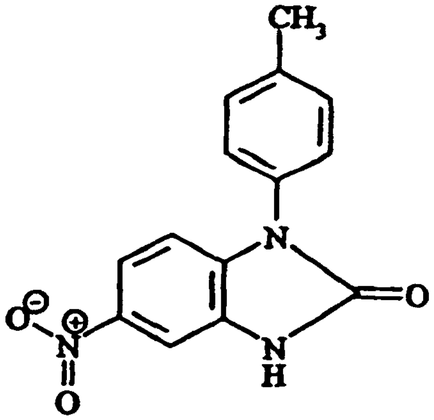
[0018] 382 parts of 2,4-dinitrophenyl-p-tolylamine are suspended in 1600 parts of ethanol and the suspension is heated to 55°C. A solution of 162 parts of sodium hydrogen sulphide hydrate in 300 parts of water is added dropwise over 2 hours. The mixture is subsequently stirred under reflux for 2 hours and then cooled to room temperature and filtered, and the filter cake is washed with 600 parts of alcohol and 3000 parts of water. Drying under reduced pressure at 80°C gives 284 parts of dark red crystals of a compound of the following formula



Yield:	83%
Melting point:	156.2°C
IR (KBr):	3428 - 1587 - 1549 - 1478 - 1284 cm^{-1}
^{1}H-NMR (DMSO): δ:	2.25 (s, CH_3) - 5.37 (s, NH_2) - 6.93 (d, ^3J=9Hz, H-C6) - 7.05 (d, ^3J=9Hz, 2H-C_{tolyl}) - 7.15 (d, ^3J=9HZ, 2H-C_{tolyl}) - 7.42 (dd, ^3J=9Hz, ^4J=2Hz, H-C5) - 7.55 (d, ^4J=2Hz, H-C3) - 7.70 (s, NH)
MS (m/e):	243 - 228 - 213 - 196 - 182 - 168 - 154 - 142 - 130

c) 5-nitro-1-p-tolyl-1,3-dihydrobenzimidazol-2-one

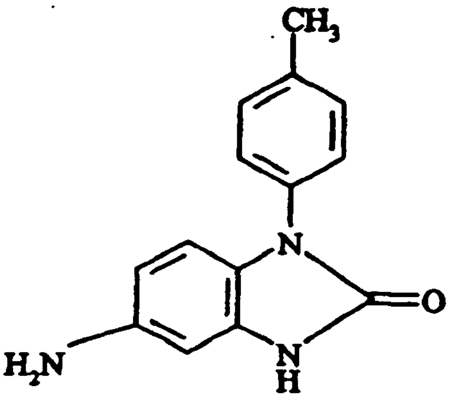
[0019] 221 parts of 4-nitro-N-1-p-tolyl-1,2-diaminobenzene and 72 parts of urea are heated with stirring at 165°C in 780 parts of o-dichlorobenzene for 4.5 hours. The mixture is subsequently cooled to room temperature and filtered and the solid product is washed with 400 parts of o-dichloro-benzene, 400 parts of methanol and 1000 parts of water. Drying under reduced pressure at 80°C gives 234 parts of beige crystals as a compound of the following formula



Yield:	97%
Melting point:	>300°C
IR (KBr):	3033 - 1725 - 1518 - 1488 - 1392 - 1343 cm^{-1}
^{1}H-NMR (DMSO): δ:	2.40 (s, CH_3) - 7.06 (d, ^3J=9Hz, H-C7) - 7.38 (d, ^3J=9Hz, 2H-C_{tolyl}) - 7.41 (d, ^3J=9Hz, 2H-C_{tolyl}) - 7.83 (d, ^4J=2Hz, H-C4) - 7.95 (dd, ^3J=9Hz, ^4J=2Hz, H-C6) - 11.50 (s, H-N3)

d) 5-amino-1-p-tolyl-1,3-dihydrobenzimidazol-2-one

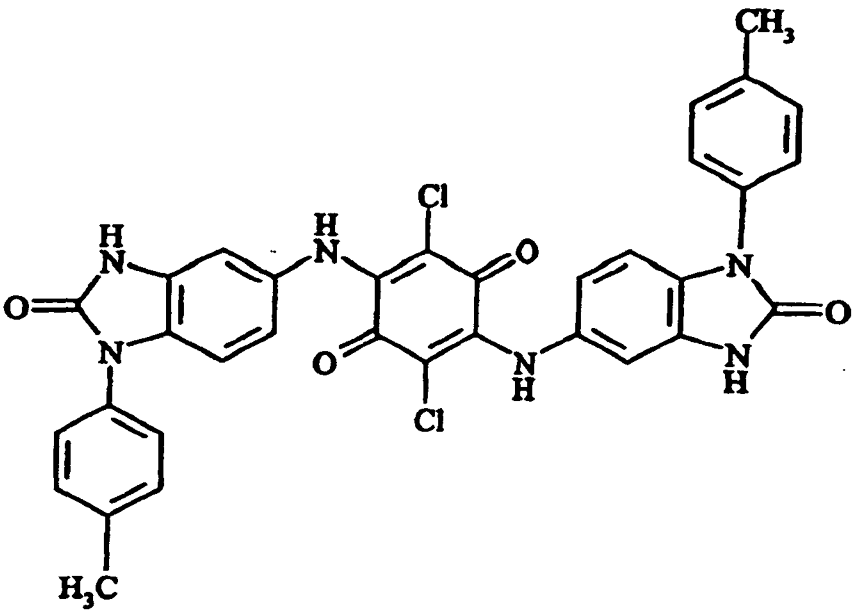
[0020] 84 parts of iron dust and 14 parts of hydrochloric acid (36%) are heated under reflux in 700 parts of water for 1 hour. 64 parts of 5-nitro-1-p-tolyl-1,3-dihydrobenz-imidazol-2-one are added over 7 hours and the mixture is subsequently stirred at this temperature for 15 hours. The mixture is then rendered alkaline with 53 parts of aqueous sodium hydroxide solution (30%), filtered to remove iron oxide, and subsequently washed with 200 parts of boiling water. Hydrochloric acid is added to adjust the filtrate to a pH of 6.5, and this filtrate is then cooled under nitrogen. The precipitated product is filtered and dried under reduced pressure at 120°C. This gives 24 parts of a pink powder of a compound of the following formula



Yield:	43%
Melting point:	245-246°C
IR (KBr):	3359 - 3134 - 1690 - 1637 - 1610 - 1519 - 1480 - 1396 cm^{-1}
^{1}H-NMR (DMSO): δ:	2.34 (s, CH_3) - 4.84 (s, NH_2) - 6.24 (dd, ^{3}J=9Hz, ^{4}J=2Hz, H-C6) - 6.46 (d, ^{4}J=2Hz, H-C4) - 6.67 (d, ^{3}J=9Hz, H-C7) - 7.30 (d, ^{3}J=9Hz, H-C2', H-C6') - 7.35 (d, ^{3}J=9Hz, H-C3', H-C5') - 10.68 (s, H-N3)
MS (m/e):	239 - 210 - 196 - 182 - 168 - 148 - 121

e) 2,5-dichloro-3,6-bis(1-p-tolyl-2-oxo-1,3-dihydrobenz-imidazol-5-ylamino)[1,4]benzoquinone

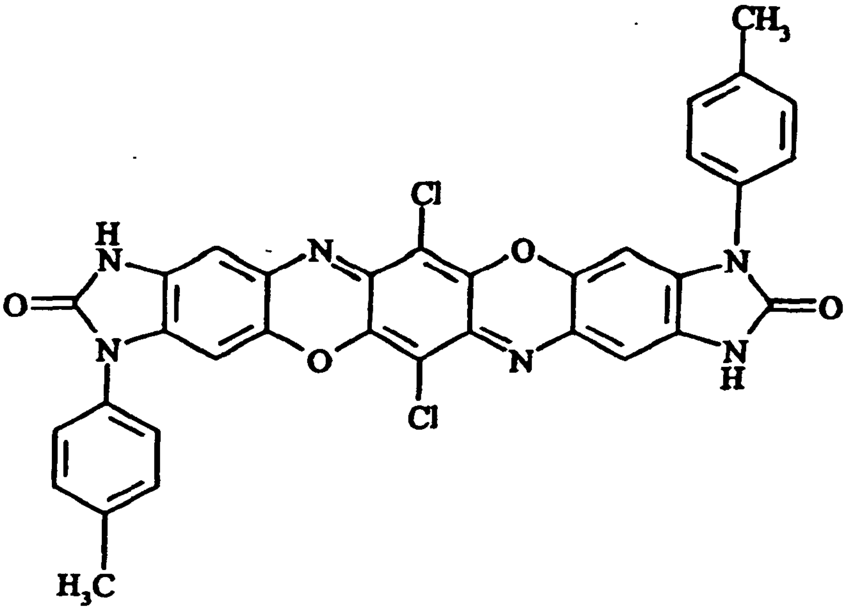
[0021] 7.4 parts of sodium acetate and 21.5 parts of 5-amino-1-p-tolyl-1,3-dihydrobenzimidazol-2-one are suspended in 160 parts of ethanol and the suspension is heated to 60°C. 11.2 parts of chloranil are added over 3 hours and the mixture is subsequently refluxed for 1 hour. The solid product is filtered off hot and washed first with 400 parts of boiling ethanol and then with 300 parts of boiling water. After drying, the product is suspended in 250 parts of dimethylformamide, the suspension is heated at 90°C for 5 hours and filtered while hot, and the solid product is washed first with 500 parts of hot (100°C) dimethylformamide and then with 300 parts of water. Drying under reduced pressure at 80°C gives 20 parts of a brown powder of a compound of the following formula



Yield:	69% .
Melting point:	>300°C
IR (KBr):	3100 (1) - 1696 - 1587 - 1491 - 1385 cm^{-1}
^1H-NMR (DMSO): δ:	2.40 (s, CH_3) - 6.83 (d, ^3J=9Hz, H-C6 or H-C7) - 6.89 (d, ^3J=9Hz, H-C6 or H-C7) - 6.91 (s, H-C4) - 7.30 (d, ^3J=9Hz, $2H_{tolyl}$) - 7.41 (d, ^3J=9Hz, $2H_{tolyl}$) - 9.64 (s, NH) - 11.17 (s, NHCO)

f) Diimidazolone(4,5-b:4',5'-m)triphendioxazine-3,11-di-p-tolyl-6,14-dichloro-2,10-dione

[0022] 180 parts of sulphuric acid (92%) are cooled to 5°C and 17 parts of 2,5-dichloro-3,6-bis(1-p-tolyl-2-oxo-1,3-dihydro-benzimidazol-5-ylamino)-[1,4]-benzoquinone are added over 30 minutes. Then 6.1 parts of activated manganese dioxide (88%) are added over 3 hours and the mixture is subsequently heated at room temperature for 12 hours. The mixture is diluted to 80% by adding 27 parts of water, with cooling. The excess manganese dioxide is destroyed using 1.2 parts of hydrogen peroxide (30%). The product is filtered off on a polypropylene filter, washed first with 250 parts of sulphuric acid (80%) and then 250 parts of sulphuric acid (50%), and subsequently washed free from sulphate with water. Drying under reduced pressure at 80°C gives 12.9 parts of a metallic-green powder of a compound of the following formula



Yield:	77%
Melting point:	>300°C
IR (KBr):	3019 (1) - 1712 - 1647 - 1562 - 1480 - 1309 - 1263 cm^{-1}

Microanalysis:

calc.	C 63.07	H 3.11	N 12.98	Cl 10.95	O 9.88
exp.	C 62.6	H 3.2	N 13.0	Cl 11.2	O 10.0

[0023] Using the method described in Example 1 further derivatives of similar 1,3-dihydrobenzimidazol-2-ones can be prepared as illustrated in Example 2.

EXAMPLE 2

Derivatives of 1-(4-methoxyphenyl)-1,3-dihydrobenzimidazol-2-one

a) 2,4-dinitrophenyl-(4-methoxyphenyl)amine

b) N-1-(4-methoxyphenyl)-4-nitro-1,2-diaminobenzene

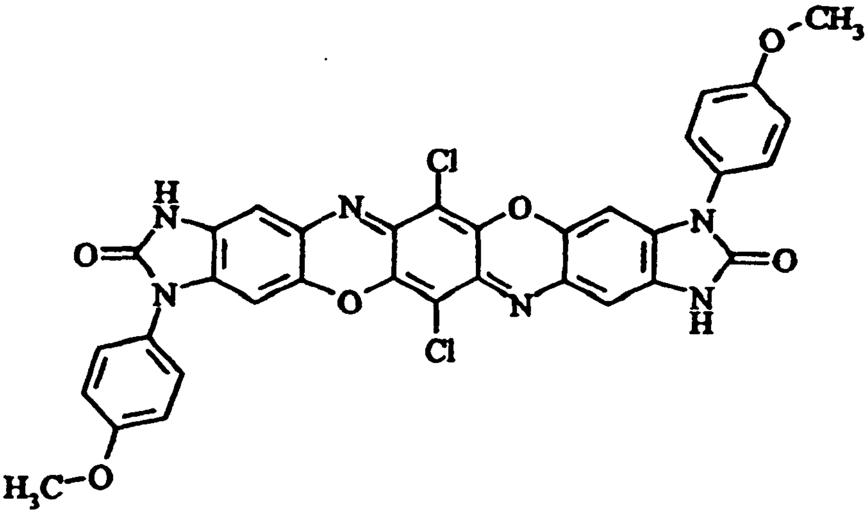
c) 1-(4-methoxyphenyl)-5-nitro-1,3-dihydrobenzimidazol-2-one

d) 5-amino-1-(4-methoxyphenyl-1,3-dihydrobenzimidazol-2-one

e) 2,5-dichloro-3,6-bis(4-methoxyphenyl-2-oxo-1,3-dihydro-benzimidazol-5-ylamino)[1,4]benzoquinone

f) Diimidazolone(4,5-b:4',5'-m)triphendioxazine-3,11-di(4-methoxyphenyl)-6,14-dichloro-2,10-dione

[0024] of the following formula



Yield:	70%
Melting point:	>300°C
IR (KBr):	3437 (1) - 1702 - 1515 - 1479 - 1313 - 1257 cm^{-1}
^{1}H-NMR (DMSO+NaOD): δ:	2.76 and 2,92 (s, CH_3) - 6.87 (s, H-Car) - 7.01 and 7.36 (d, ^3J=9Hz, 2H-C_{PhOMe}) - 7.03 (s, H-Car) - 7.05 and 7.38 (d, ^3J=9Hz, 2H-C_{PhOMe})

USE EXAMPLE 3

[0025]

4 parts	of the pigment set out in the table below are milled in a ball mill with
96 parts	of a mixture of
50 parts	of a 60 per cent strength solution of coco-aldehyde-melamine resin solution in butanol,
10 parts	of xylene and
10 parts	of ethylene glycol monoethyl ether for 24 hours.

[0026] The resulting dispersion is sprayed onto sheet aluminium, left to dry in air for 30 minutes and then baked at 120°C for 30 minutes. The result is a film of the colour specified in the table below, with very good migration fastness and also good light and weathering stability.

USE EXAMPLE 4

[0027] Example of the preparation of a 0.1% coloured PVC film (blend of colour pigment to white pigment 1:5):

16.5 parts	of a plasticizer mixture consisting of equal parts of dioctyl phthalate and dibutyl phthalate are mixed with
0.05 parts	of the pigment set out in the table below and with
0.25 parts	of titanium dioxide. Then
33.5 parts	of polyvinyl chloride are added.

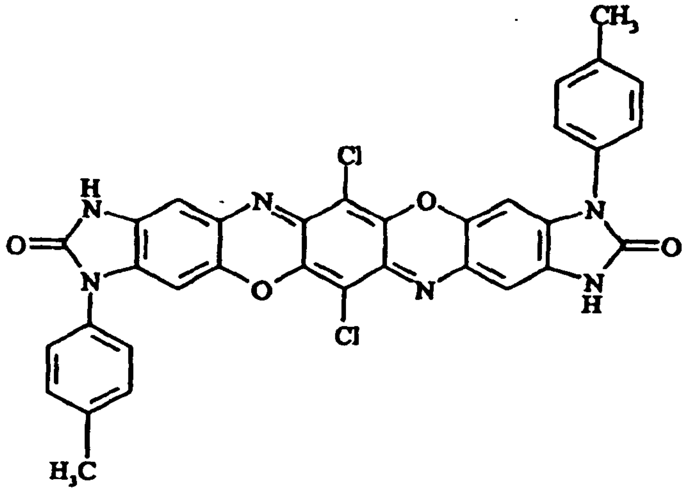
[0028] The mixture is friction-rolled on a double-roll mill for 10 minutes, the resulting sheet being continually cut with a spatula and rolled together. In the roll mill, one roll is held at a temperature of 40° and the other at a temperature of 140°. The mixture is subsequently taken off in sheet form and pressed between two polished metal plates at 160° for 5 minutes. This gives a coloured PVC film of high brightness and very good migration and light fastness.

TABLE

Pigment of Example	Colour in Use Example 3	Colour in Use Example 4
1 f	violet	violet
2 f	violet	violet

Claims

1. Triphendioxazine compounds of the general formulae (1f) or (2f)



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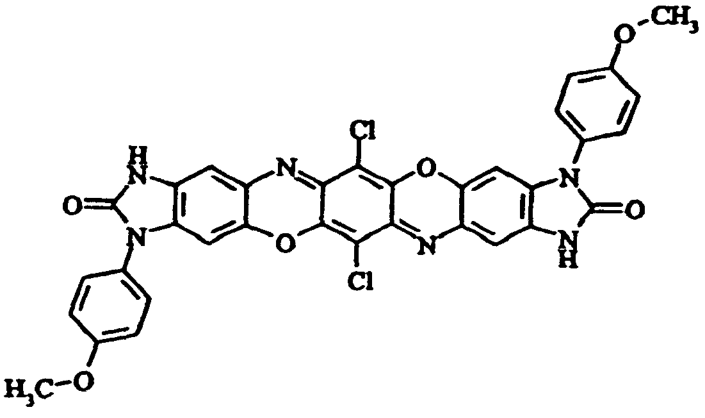


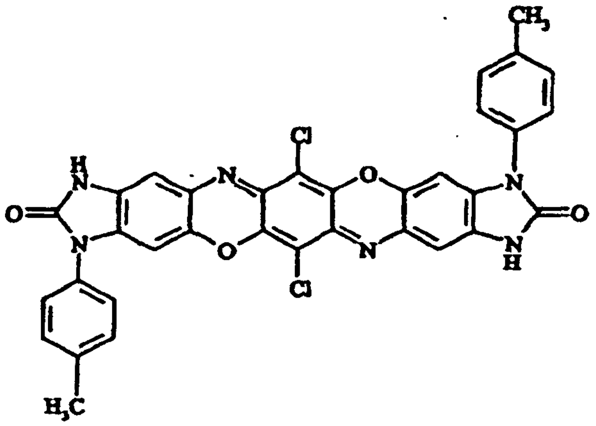
(2f)

2. Use of the compounds of the formulae (1f) or (2f) according to claim 1 as pigments.

3. Use of the compounds of the formulae (1f) or (2f) according to claim 1 as colorants for colouring polymer compositions or paper pulps, as colorants in electrophotographic toners and developers, as colorants in ink-jet inks, as colorants in the coatings industry, as colorants for textile printing or as a printing ink in the graphical industry.

Patentansprüche

1. Triphendioxazinverbindungen der allgemeinen Formeln (1f) oder (2f)



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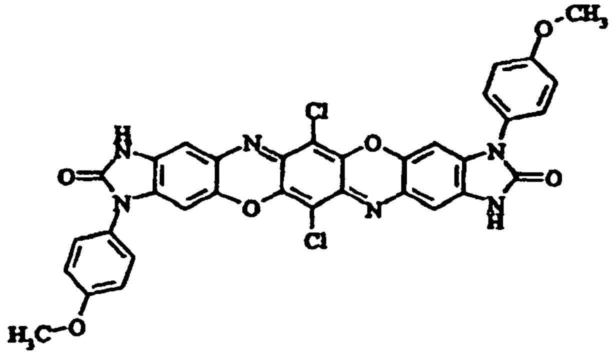


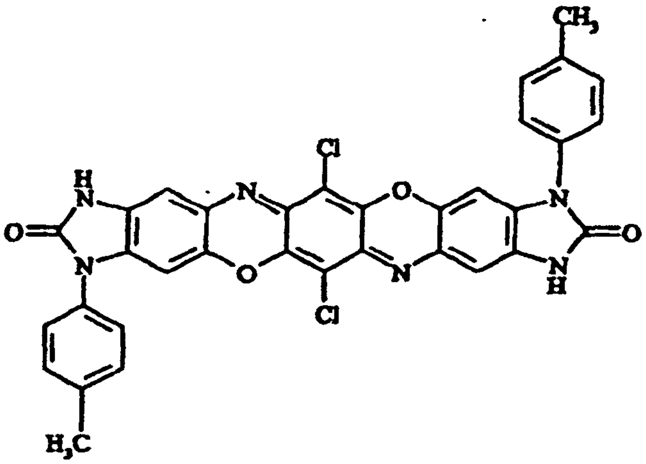
(2f)

2. Verwendung der Verbindungen der Formeln (1f) oder (2f) gemäß Anspruch 1 als Pigmente.

3. Verwendung der Verbindungen der Formeln (1f) oder (2f) gemäß Anspruch 1 als Farbmittel zum Färben von Kunststoff- oder Papiermassen, als Farbmittel in elektrophotographischen Tonern und Entwicklern, als Farbmittel in Ink-Jet-Tinten, als Farbmittel in der Lackindustrie, als Farbmittel für den Textildruck oder als Druckfarbe im graphischen Gewerbe.

Revendications

1. Composés de triphéndioxazine de formules générales (1f) ou (2f)



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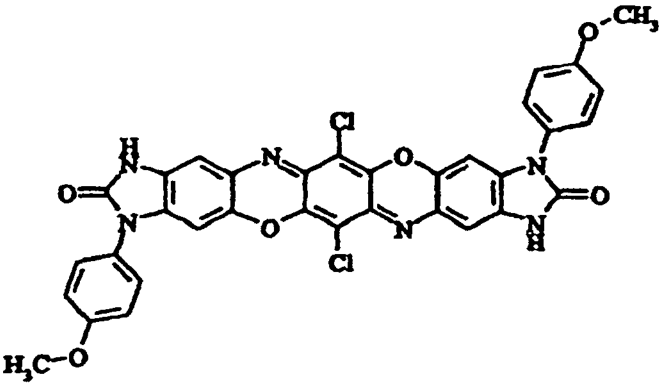

(2f)

2. Utilisation des composés de formules (1f) ou (2f) selon la revendication 1 comme pigments.

3. Utilisation des composés de formules (1f) ou (2f) selon la revendication 1 comme colorants pour la coloration de compositions de polymères ou de pâtes à papier, comme colorants dans des révélateurs et des toners électrophotographiques, comme colorants dans des encres pour jet d'encre, comme colorants dans l'industrie des revêtements, comme colorants pour l'impression de textiles ou comme encre d'impression dans l'industrie graphique.